ELECTROCHEMICAL STUDIES OF SOME COORDINATION COMPOUNDS OF SILVER

BY

ALAN LINDSEY McCLELLAND

B.S., Northwestern University, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ACKNOWLEDGMENT

The author very gratefully acknowledges the help and encouragement given by Dr. J. C. Bailar, Jr., both in the direction of this work and throughout the author's residence at the University of Illinois. The suggestions and help of Dr. H. A. Laitinen are also greatly appreciated.

Financial assistance was kindly provided by the Burgess Battery Co. and Graham, Crowley, and Associates through a research fellowship, and by the Atomic Energy Commission, also through a research fellowship.

The author is also deeply indebted to his wife for her patience and encouragement throughout the course of this work.

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I. Introduction

Though the preparation of numerous compounds of di- and tri-valent silver has been reported in the literature, relatively few quantitative data are available on the stability of these compounds. It was the purpose of this study, therefore, to obtain such data, in the form of oxidation potentials and dissociation constants, for some of the coordination compounds of divalent silver. Such data should be useful in clarifying the relationships of the elements of the copper subgroup of the periodic table, in predicting the stability of other compounds of divalent silver, and in indicating possible uses and reactions of these compounds.

The general method used was based on the measurement of the potential of the silver(I)-silver(II) couple in the presence of varying concentrations of the complexing agent, and from these values and similar data for the corresponding silver-silver(I) system, calculation of the formulas and dissociation constants of the complex ions, and the standard potentials of the systems involved. Complexing agents studied were pyridine, dipyridyl, and 1,10-phenanthroline.

II. Historical

Many compounds of di- and tri-valent silver have been prepared and well characterized in the solid state (1,7). The most extensively studied have been the divalent oxide, AgO, the divalent fluoride, AgF_2, and the black compound usually given the formula $Ag_7O_8NO_3$. Other compounds reported include the trivalent oxide, Ag_2O_3, never obtained in the pure state, coordination compounds of trivalent silver with periodate ion and with ethylenebiguanide, and coordination compounds of divalent silver with pyridine, dipyridyl, tripyridyl, 1,10-phenanthroline, picolinic acid, and quinolinic acid.

The only oxidizing agents which are known to oxidize silver to higher valence states are ozone, fluorine, peroxydisulfates, and lead dioxide. Electrolytic oxidation has also been successful.

Most of the coordination compounds of divalent silver have an apparent coordination number of four, and in the case of the inner complex with picolinic acid, x-ray examination has shown that the four bonds are coplanar (5). This is in agreement with the dsp^2 bonding which might logically be expected for di-valent silver.

Morgan and Burstall (9), however, report the preparation of *tris*-dipyridylsilver(II) nitrate, chlorate, and perchlorate, as well as the *bis*-dipyridylsilver(II) peroxydisulfate and hydrogen sulfate. Thus it appears that silver(II) may also have a coordination number of six. The coordination number of six in these complexes is analogous to that in the *tris*-dipyridylcopper(II) complexes studied by Onstott (11). *Bis*-dipyridylsilver(II) nitrate was prepared electrolytically by Barbieri (4).

Barbieri (2) first prepared tetrapyridinesilver(II) peroxydisulfate, an insoluble, reddish-orange salt, by the action of potassium peroxydisulfate on an aqueous solution of silver nitrate and pyridine. The reaction is rapid at room temperature, yielding an easily filterable precipitate which when washed and dried is indefinitely stable. He later prepared the corresponding nitrate in very small amounts by electrolytic oxidation of a solution of silver nitrate and pyridine (3). He reported this compound to be unstable in the solid state.

Hieber and Muhlbauer (6) prepared a series of *bis*-1,10-phenanthrolinesilver(II) salts, including the peroxydisulfate, perchlorate, chlorate, nitrate, and hydrogen sulfate. These were obtained by oxidation with potassium peroxydisulfate and subsequent metathesis. Pfeiffer (12) studied the conditions for the preparation of the complex of monovalent silver, *bis*-1,10-phenanthrolinesilver(I) nitrate, and

found that it was easily obtained in a crystalline form by recrystallization from nitrobenzene. He also prepared *tris*-1, 10-phenanthrolinesilver(I) perchlorate.

Noyes, *et al*, (10) made an extensive study of the nature and stability of the ions present in solutions of divalent silver in nitric and perchloric acids. They found that oxidation with ozone or by electrolysis produced solutions containing the silver almost exclusively in the mono-and di-valent states, though a small amount of trivalent silver, probably in the form of AgO^+ ions, was present in equilibrium with the lower valence states. They suggested as a possible equation for the equilibrium

$$2\ Ag^{++} + H_2O = AgO^+ + Ag^+ + 2\ H^+.$$

The divalent silver in nitric acid is complexed to some extent by nitrate ion, as indicated by the change of potential of the silver(I)-silver(II) system with changing nitrate ion concentration, by the difference in color of solutions of divalent silver in nitric and perchloric acids, and by the fact that transference experiments show some of the silver to be anionic.

The kinetics of the oxidation of silver nitrate solutions in nitric acid by ozone were studied, and the rate of oxidation of the silver was found to be directly proportional to the ozone and monovalent silver concentrations and practically independent of acid concentration and ionic strength. The kinetics of the reaction by which the divalent silver oxidizes water to oxygen were also studied. The rate of reduction was found to be largely second order with respect to divalent silver, with a small fourth order contribution, and first order with respect to monovalent silver. The reduction rate was also observed to be greatly diminished by increasing acid concentration and to have a temperature coefficient very much larger than that of most reactions.

The oxidation potentials of the silver(I)-silver(II) system were measured in four molar nitric and perchloric

acids. At 25.0°C. the values found were 1.93 and 2.00 volts *vs.* the hydrogen electrode for nitric and perchloric acids respectively. The value for perchloric acid solution was later revised to 1.97 volts (8).

III. Experimental

In the study of the pyridine complexes of divalent silver, electrolytic oxidation was first used to prepare solutions of the divalent complexes, but this method proved unsatisfactory because of the low yields of divalent silver obtained. This low current efficiency was due to the establishment of a steady state in which the divalent silver oxidized some other component of the solution as rapidly as it was being formed by the electrolytic oxidation. Dissolution of divalent silver oxide in 7M nitric acid and addition of a small amount of the resulting solution to a large excess of aqueous pyridine was found to be a suitable way of preparing solutions of the divalent complexes. The potential of a platinum electrode in these solutions was measured to determine the potential of the silver(I)-silver(II) couple in the presence of pyridine.

An amperometric titration procedure was developed for determination of divalent silver concentration. The sample of silver solutions was added to an excess of standard sodium arsenite solution, and the excess arsenite back-titrated amperometrically with ceric sulfate in 1N sulfuric acid, using osmic acid solution as a catalyst. Total silver determination was made gravimetrically as the chloride.

Since the divalent silver in these solutions continually oxidized some other component of the solution, the concentration of the divalent silver decreased with time. The rate of this reaction was determined by measuring the rate of change of optical density at 4080 Angstroms, of reduction current at a rotating platinum electrode at + 0.4 volts *vs.* the saturated calomel electrode, and of concentration as determined by titration of samples withdrawn at regular intervals.

Ceric ammonium nitrate in 1M nitric acid was found to

oxidize silver quantitatively to the divalent state in the presence of dipyridyl. Therefore, the potential of the silver(I)-silver(II) couple involving the dipyridyl complexes was determined by making potentiometric titrations with standard solutions of ceric ammonium nitrate in nitric acid adjusted to pH 0.00 of standard solutions of silver nitrate containing known amounts of dipyridyl and adjusted to pH 0.00. The concentrations of mono-and di-valent silver at each point on the titration curves were calculated from the original concentration of silver and the amount of ceric nitrate solution added. The concentration of dipyridyl at each point was calculated from the original concentration and the volume increase.

The investigation of the 1,10-phenanthroline complexes of silver could not be carried out by the method used for the dipyridyl complexes of silver because of the unusual solubility relationships of the monovalent 1,10-phenanthroline complexes. *Bis*-1,10-phenanthroline silver(I) nitrate is one of the least soluble of the salts of the *bis*-1,10-phenanthroline silver (1) cation with the common anions. The perchlorate and nitrite are also insoluble, but the chloride, sulfate, carbonate, fluoride, and hydroxide are all soluble. Therefore, the compositions of the 1,10-phenanthroline complexes were studied by dissolving AgO in 1N sulfuric acid containing a known amount of 1,10-phenanthroline and adjusted to pH 0.00. The solutions were then progressively diluted with sulfuric acid of pH 0.00, thereby changing the ratio of divalent to monovalent silver. The divalent silver concentration was determined by the method used for the divalent pyridine complexes. Total silver concentration was calculated from the amount of AgO added.

IV. Discussion and Results

Pyridine was found to form two complex ions with divalent silver, having the composition *tris*-pyridinesilver(II) ion and *tetrakis*-pyridinesilver(II) ion. The dissociation constants of the two ions were found to be 10^{-14} and10^{-15},

respectively. The standard potential of the pyridine complexes of mono- and di-valent silver is 1.33 volts vs. the hydrogen electrode at 25°C. These values are based on the actual concentration of pyridine molecules as calculated from the total pyridine concentration, the pH, and the base dissociation constant of pyridine.

The silver(II)-pyridine complex ions are not stable in solution, being completely reduced to the monovalent state within a few hours. The reduction reaction was found to be predominately first order with respect to divalent silver, though some higher order reaction apparently contributes to the rate in the early stages of the reaction. The first order rate constant appears to be little affected by changes in pyridine concentration.

Dipyridyl forms *bis*-dipyridylsilver(II) ion in 1M HNO_3 solution. This ion is formed by oxidation of monovalent silver by ceric ammonium nitrate in nitric acid. The dissociation constant of the ion is 2.5×10^{-19} and the standard potential of the dipyridyl complexes of monovalent and divalent silver is 0.814 volts vs. the hydrogen electrode at 25°C. This value is based on the concentration of dipyridyl molecules calculated from the total dipyridyl concentration, the pH, and the base dissociation constant of dipyridyl. A new compound of divalent silver, *bis*-dipyridylsilver(II) ceric nitrate, having the formula $[Ag\ dipy_2]\ (NO_3)_2 . Ce(NO_3)_4$ was found to precipitate after the end point of the titration.

1,10-phenanthroline forms monovalent silver complexes with unusual solubility relationships, the nitrate, perchlorate, and nitrite being insoluble, and the fluoride, chloride, carbonate, and hydroxide being soluble. In 0.5 M sulfuric acid solution ceric sulfate solutions will not oxidize silver quantitatively to the divalent state, but will oxidize it partially. The variation of the formal potential of the silver(I)-silver (II) couple with change in phenanthroline concentration is not a linear function of the logarithm of the phenanthroline concentration, indicating a change in the average number of

phenanthroline molecules complexed to the mono- or di-valent silver ions. This makes it impossible to accurately extrapolate to the value for the standard potential of the phenanthroline complexes of mono- and di-valent silver, but 1.3 volts *vs.* the hydrogen electrode at 25°C. is an approximate value. This value is based on the total phenanthroline concentration in the solution, and provided that phenanthroline and dipyridyl have approximately the same strength as bases, the divalent silver complex of phenanthroline is of approximately the same stability as the dipyridyl complex.

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VITA

Alan Lindsey McClelland was born on September 19, 1925 in Galesburg, Illinois. He attended the public schools of that city, graduating from Galesburg High School in 1943, after which he enlisted in the Navy. During 1944 and 1945 he attended Ohio Wesleyan and Northwestern Universities while on active duty in the Navy V-12 and Reserve Officers' Training Corps Programs. He received the degree of Bachelor of Science from Northwestern University and a commission as an ensign in the Naval Reserve in 1945. After 9 months more duty in the Navy he was released to inactive duty in August 1946. He entered the University of Illinois in the fall of 1946 as an unclassified student, and entered the Graduate School in the summer of 1947. During the second semester of 1946-47 and during the academic year 1948-49, the author served as a teaching assistant in the Inorganic Division of the Chemistry Department. He held a Graham, Crowley, and Associates research fellowship for one year beginning in August 1947, and an Atomic Energy Commission Predoctoral Fellowship for one year beginning in June 1949.

The author married Janet Ann Wynn, of Galesburg, Illinois in 1947, and they now have one child, Steven Wynn.

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